IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of Hajime KONDO
Application No.: 10/558,389
Filed: November 29, 2005
For: MODIFIED NATURAL RUBBER OR MODIFIED NATURAL RUBBER LATEX, AND RUBBER COMPOSITION AND PNEUMATIC TIRE
Group Art Unit: 1796
Examiner: Peter D. Mulcahy
Confirmation No.: 5714

DECLARATION UNDER 37 C.F.R. § 1.132

I, Makiko Yonemoto, declare that:

I am a co-worker of Mr. Hajime Kondo who is the inventor of the above-captioned patent application.

I received my Master of Science and Engineering from Tokyo Institute of Technology in 2004, and have been employed by Bridgestone Corporation since 2004, where I have been engaged mainly in research and development of new natural rubber.

I have made the following experiments in order to evaluate the Mooney viscosity, the ultimate strength (fracture resistance), the crack growth resistance and the tan δ of the rubber composition comprising the modified natural rubber, which is obtained by graft-polymerizing natural rubber latex with a polar group-containing monomer and then coagulating and drying, and carbon black and/or silica, wherein a grafting ratio of the polar group-containing monomer is 0.01-5.0% by mass per the natural rubber latex, and a content of the modified natural rubber in a rubber component of the rubber composition is at least 15% by mass. Further, I have made the following experiments in order to evaluate the rolling resistance of the tire using the above rubber composition.

Experimental Procedure

<Production Example of Modified natural rubber A-1>

A modified natural rubber A-1 is obtained in the same manner as in Production Example 1 described in the present specification. As the modified natural rubber A-1 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this

example, 3.0 g of N,N-diethylaminoethyl methacrylate is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 3.0/600 = 0.5%.

<Production Example of Modified natural rubber A-2>

A modified natural rubber A-2 is obtained in the same manner as in Production Example 1 described in the present specification except that 28.2 g of N,N-diethylaminoethyl methacrylate is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber A-2 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 28.2 g of N,N-diethylaminoethyl methacrylate is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 28.2/600 = 4.7%.

<Production Example of Modified natural rubber A-3>

A modified natural rubber A-3 is obtained in the same manner as in Production Example 1 described in the present specification except that 34.8 g of N,N-diethylaminoethyl methacrylate is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber A-3 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 34.8 g of N,N-diethylaminoethyl methacrylate is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 34.8/600 = 5.8%.

<Production Example of Modified natural rubber A-4>

A modified natural rubber A-4 is obtained in the same manner as in Production Example 1 described in the present specification except that 42.0 g of N,N-diethylaminoethyl methacrylate is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber A-4 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 42.0 g of N,N-diethylaminoethyl methacrylate is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 42.0/600 = 7.0%.

<Production Example of Modified natural rubber B-1>

A modified natural rubber B-1 is obtained in the same manner as in Production Example 1 described in the present specification except that 3.0 g of 2-hydroxyethyl methacrylate is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber B-1 is analyzed in the same manner as in Production Example 1 described in the present specification,

it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 3.0 g of 2-hydroxyethyl methacrylate is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 3.0/600 = 0.5%.

<Production Example of Modified natural rubber B-2>

A modified natural rubber B-2 is obtained in the same manner as in Production Example 1 described in the present specification except that 26.4 g of 2-hydroxyethyl methacrylate is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber B-2 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 26.4 g of 2-hydroxyethyl methacrylate is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 26.4/600 = 4.4%.

<Production Example of Modified natural rubber B-3>

A modified natural rubber B-3 is obtained in the same manner as in Production Example 1 described in the present specification except that 31.2 g of 2-hydroxyethyl methacrylate is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber B-3 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 31.2 g of 2-hydroxyethyl methacrylate is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 31.2/600 = 5.2%.

<Production Example of Modified natural rubber B-4>

A modified natural rubber B-4 is obtained in the same manner as in Production Example 1 described in the present specification except that 42.0 g of 2-hydroxyethyl methacrylate is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber B-4 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 42.0 g of 2-hydroxyethyl methacrylate is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 42.0/600 = 7.0%.

<Production Example of Modified natural rubber F-1>

A modified natural rubber F-1 is obtained in the same manner as in Production Example 1 described in the present specification except that 3.0 g of acrylonitrile is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber F-1 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 3.0 g of acrylonitrile is added to 600 g of latex (60% of 1000 g of the concentrated

latex), so that the grafting ratio is 3.0/600 = 0.5%.

<Production Example of Modified natural rubber F-2>

A modified natural rubber F-2 is obtained in the same manner as in Production Example 1 described in the present specification except that 27.0 g of acrylonitrile is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber F-2 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 27.0 g of acrylonitrile is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 27.0/600 = 4.5%.

<Production Example of Modified natural rubber F-3>

A modified natural rubber F-3 is obtained in the same manner as in Production Example 1 described in the present specification except that 33.0 g of acrylonitrile is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber F-3 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 33.0 g of acrylonitrile is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 33.0/600 = 5.5%.

<Production Example of Modified natural rubber F-4>

A modified natural rubber F-4 is obtained in the same manner as in Production Example 1 described in the present specification except that 42.0 g of acrylonitrile is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber F-4 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 42.0 g of acrylonitrile is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 42.0/600 = 7.0%.

<Production Example of Modified natural rubber O-1>

A modified natural rubber O-1 is obtained in the same manner as in Production Example 1 described in the present specification except that 0.6 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-1 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 0.6 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 0.6/600 = 0.1%.

<Production Example of Modified natural rubber O-2>

A modified natural rubber O-2 is obtained in the same manner as in Production Example 1 described in the present specification except that 3.0 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-2 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 3.0 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 3.0/600 = 0.5%.

<Production Example of Modified natural rubber O-3>

A modified natural rubber O-3 is obtained in the same manner as in Production Example 1 described in the present specification except that 28.8 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-3 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 28.8 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 28.8/600 = 4.8%.

<Production Example of Modified natural rubber O-4>

A modified natural rubber O-4 is obtained in the same manner as in Production Example 1 described in the present specification except that 60.0 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-4 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 60.0 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 60.0/600 = 10%.

<Production Example of Modified natural rubber O-5>

A modified natural rubber O-5 is obtained in the same manner as in Production Example 1 described in the present specification except that 90.0 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-5 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 90.0 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 90.0/600 = 15%.

<Production Example of Modified natural rubber O-6>

A modified natural rubber O-6 is obtained in the same manner as in Production Example

1 described in the present specification except that 33.0 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-6 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 33.0 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 33.0/600 = 5.5%.

<Production Example of Modified natural rubber O-7>

A modified natural rubber O-7 is obtained in the same manner as in Production Example 1 described in the present specification except that 42.0 g of 2-vinylpyridine is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-7 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 42.0 g of 2-vinylpyridine is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 42.0/600 = 7.0%.

<Production Example of Modified natural rubber U-1>

A modified natural rubber U-1 is obtained in the same manner as in Production Example 1 described in the present specification except that 126.0 g of γ-methacryloxypropyl trimethoxy silane is used instead of 3.0 g of N,N-diethylaminoethyl methacrylate. As the modified natural rubber O-1 is analyzed in the same manner as in Production Example 1 described in the present specification, it is confirmed that 100% of the monomer added is introduced into the natural rubber molecule. In this example, 126.0 g of γ-methacryloxypropyl trimethoxy silane is added to 600 g of latex (60% of 1000 g of the concentrated latex), so that the grafting ratio is 126.0/600 = 21%.

<Preparation of Rubber composition>

A rubber composition is prepared by using the modified natural rubber A-1, A-2, A-3, A-4, B-1, B-2, B-3, B-4, F-1, F-2, F-3, F-4, O-1, O-2, O-3, O-4, O-5, O-6, O-7 or U-1, respectively, according to a compounding recipe shown in the following Tables I, II, III, IV, V and VI. With respect to the resulting rubber composition, the Mooney viscosity, the ultimate strength (fracture resistance), the crack growth resistance and the tan δ are evaluated according to the following methods. Further, with respect to a tire prepared by using the rubber composition, the rolling resistance is evaluated according to the following method. Results are shown in Tables I, II, III, IV, V and VI.

(1) Mooney viscosity

For evaluating the processability of the rubber compositions, unvulcanized rubber

samples were kneaded together with a vulcanized ingredient and preheated at 130°C for 1 minute using "MOONY VISCOMETER SMV201" manufactured by Shimadzu Co., Ltd., and then the rotation of the rotor was started, and the value after a lapse of 4 minute was measured as ML_{1+4}. The higher the value, the higher the unvulcanized viscosity and lower the processability or productivity.

(2) Ultimate strength (fracture resistance)

A specimen vulcanized at 160°C for 20 minutes was measured in accordance with JIS K6251-1993 to determine the tensile strength at 23°C. The higher the value, the higher the fracture resistance.

(3) Crack growth resistance

Dumbbell-shaped specimens were punched out of a rubber composition vulcanized under vulcanization conditions at 160°C for 10 minutes, and the specimens having formed a preliminary crack of 5 mm at the center thereof were mounted on a fatigue testing machine, and subjected to strokes at 7 Hz at a constant stress, a temperature of 80°C, and a chuck distance of 20 mm, and the number of cycles necessary to a complete fracture was represented as an index on the basis that the case of Additional Comparative Example 5 is 100. The higher the value, the longer the life and the better the crack growth resistance.

(4) tan δ

Measurements were conducted on a rubber composition vulcanized under vulcanization conditions at 160°C for 14 minutes using a spectrometer (dynamic viscoelasticity measuring testing machine), at an initial load of 160 g, a frequency of 50 Hz, a strain of 1%, and a measuring temperature of 23°C. The value was represented as an index on the basis that the case of Additional Comparative Example 5 is 100. The larger the index value, the lower the loss.

(5) Rolling resistance

A rubber composition was used as the ply coating rubber, and the rolling resistance of the tire (size: 185/70R14) was measured with a drum, and the value was represented as an index on the basis that the case of Additional Comparative Example 5 is 100. The higher the value, the better the rolling resistance and the better the low rolling resistance.

Table I

			Additional Comparative Example 1	Additional Example 8	Additional Example 9	Additional Comparative Example 11	Additional Comparative Example 12
Formulation	Natural rubber (grafting ratio=0%)	parts by mass	100	-	-	-	-
	Modified natural rubber A-1 (grafting ratio=0.5%)		-	100	-	-	-
	Modified natural rubber A-2 (grafting ratio=4.7%)		-	-	100	-	-
	Modified natural rubber A-3 (grafting ratio=5.8%)		-	-	-	100	-
	Modified natural rubber A-4 (grafting ratio=7.0%)		-	-	-	-	100
	Carbon Black		50	50	50	50	50
	Silica		-	-	-	-	-
	Spindle Oil		12	12	12	12	12
	Stearic Acid		1.5	1.5	1.5	1.5	1.5
	Zinc Oxide		4	4	4	4	4
	Vulcanization Accelerator		0.8	0.8	0.8	0.8	0.8
	Sulfur		3	3	3	3	3
Results	Mooney viscosity	-	69	69	76	79	82
	Ultimate strength	MPa	26	28	26	23	18
	Crack growth resistance	index	105	103	102	101	97
	tan δ	index	105	143	148	138	137
	Rolling resistance	index	100	105	106	102	102

* Modified natural rubbers A-1, A-2, A-3 and A-4 are a modified natural rubber graft-polymerized with N,N-diethylaminoethyl methacrylate.

Table II

			Additional Comparative Example 1	Additional Example 10	Additional Example 11	Additional Comparative Example 13	Additional Comparative Example 14
Formulation	Natural rubber (grafting ratio=0%)	parts by mass	100	-	-	-	-
	Modified natural rubber B-1 (grafting ratio=0.5%)		-	100	-	-	-
	Modified natural rubber B-2 (grafting ratio=4.4%)		-	-	100	-	-
	Modified natural rubber B-3 (grafting ratio=5.2%)		-	-	-	100	-
	Modified natural rubber B-4 (grafting ratio=7.0%)		-	-	-	-	100
	Carbon Black		50	20	20	20	20
	Silica		-	30	30	30	30
	Spindle Oil		12	12	12	12	12
	Stearic Acid		1.5	1.5	1.5	1.5	1.5
	Zinc Oxide		4	4	4	4	4
	Vulcanization Accelerator		0.8	0.8	0.8	0.8	0.8
	Sulfur		3	3	3	3	3
Results	Mooney viscosity	-	69	80	82	86	89
	Ultimate strength	MPa	26	25	23	19	17
	Crack growth resistance	index	105	100	101	99	95
	tan δ	index	105	150	156	148	147
	Rolling resistance	index	100	106	107	105	105

* Modified natural rubbers B-1, B-2, B-3 and B-4 are a modified natural rubber graft-polymerized with 2-hydroxyethyl methacrylate.

Table III

			Additional Comparative Example 1	Additional Example 12	Additional Example 13	Additional Comparative Example 15	Additional Comparative Example 16
Formulation	Natural rubber (grafting ratio=0%)	parts by mass	100	-	-	-	-
	Modified natural rubber F-1 (grafting ratio=0.5%)		-	100	-	-	-
	Modified natural rubber F-2 (grafting ratio=4.5%)		-	-	100	-	-
	Modified natural rubber F-3 (grafting ratio=5.5%)		-	-	-	100	-
	Modified natural rubber F-4 (grafting ratio=7.0%)		-	-	-	-	100
	Carbon Black		50	20	20	20	20
	Silica		-	30	30	30	30
	Spindle Oil		12	12	12	12	12
	Stearic Acid		1.5	1.5	1.5	1.5	1.5
	Zinc Oxide		4	4	4	4	4
	Vulcanization Accelerator		0.8	0.8	0.8	0.8	0.8
	Sulfur		3	3	3	3	3
Results	Mooney viscosity	-	69	81	83	86	90
	Ultimate strength	MPa	26	24	22	18	17
	Crack growth resistance	index	105	100	101	98	95
	tan δ	index	105	148	153	147	145
	Rolling resistance	index	100	105	106	105	105

* Modified natural rubbers F-1, F-2, F-3 and F-4 are a modified natural rubber graft-polymerized with acrylonitrile.

Table IV

			Additional Comparative Example 1	Additional Example 1	Additional Example 2	Additional Example 3	Additional Example 4	Additional Comparative Example 17	Additional Comparative Example 18
Formulation	Natural rubber (grafting ratio=0%)	parts by mass	100	-	-	-	-	-	-
	Modified natural rubber O-1 (grafting ratio=0.1%)		-	100	-	-	-	-	-
	Modified natural rubber O-2 (grafting ratio=0.5%)		-	-	100	-	-	-	-
	Modified natural rubber O-3 (grafting ratio=4.8%)		-	-	-	100	100	-	-
	Modified natural rubber O-6 (grafting ratio=5.5%)		-	-	-	-	-	100	-
	Modified natural rubber O-7 (grafting ratio=7.0%)		-	-	-	-	-	-	100
	Carbon Black		50	50	50	20	50	50	50
	Silica		-	-	-	30	-	-	-
	Spindle Oil		12	12	12	12	12	12	12
	Stearic Acid		1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Zinc Oxide		4	4	4	4	4	4	4
	Vulcanization Accelerator		0.8	0.8	0.8	0.8	0.8	0.8	0.8
	Sulfur		3	3	3	3	3	3	3
Results	Mooney viscosity	-	69	70	66	73	74	75	78
	Ultimate strength	MPa	26	25	27	23	24	21	19
	Crack growth resistance	index	105	100	103	108	102	101	99
	tan δ	index	105	125	140	155	146	138	137
	Rolling resistance	index	100	101	105	107	105	102	102

* Modified natural rubbers O-1, O-2, O-3, O-6 and O-7 are a modified natural rubber graft-polymerized with 2-vinylpyridine.

Table V

			Additional Comparative Example 1	Additional Comparative Example 2	Additional Comparative Example 3	Additional Comparative Example 4
Formulation	Natural rubber (grafting ratio=0%)	parts by mass	100	-	-	-
	Modified natural rubber O-4 (grafting ratio=10%)		-	100	-	-
	Modified natural rubber O-5 (grafting ratio=15%)		-	-	100	-
	Modified natural rubber U-1 (grafting ratio=21%)		-	-	-	100
	Carbon Black		50	50	50	20
	Silica		-	-	-	30
	Spindle Oil		12	12	12	12
	Stearic Acid		1.5	1.5	1.5	1.5
	Zinc Oxide		4	4	4	4
	Vulcanization Accelerator		0.8	0.8	0.8	0.8
	Sulfur		3	3	3	3
Results	Mooney viscosity	-	69	81	84	92
	Ultimate strength	MPa	26	18	17	16
	Crack growth resistance	index	105	97	95	93
	tan δ	index	105	135	130	150
	Rolling resistance	index	100	103	103	104

* Modified natural rubbers O-4 and O-4 are a modified natural rubber graft-polymerized with 2-vinylpyridine.

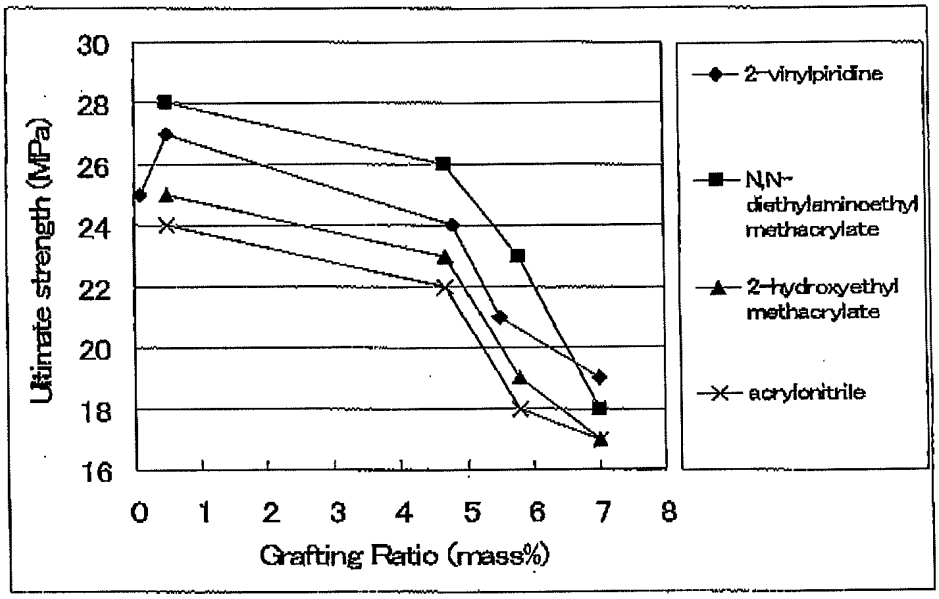
* Modified natural rubber U-1 is a modified natural rubber graft-polymerized with γ-methacryloxypropyl trimethoxy silane.

Table VI

			Additional Comparative Example 5	Additional Comparative Example 6	Additional Example 5	Additional Comparative Example 7	Additional Example 6	Additional Comparative Example 8	Additional Example 7	Additional Comparative Example 9	Additional Comparative Example 10
Formulation	Natural rubber (grafting ratio=0%)	parts by mass	70	70	-	40	-	20	-	10	-
	Modified natural rubber O-2 (grafting ratio=0.5%)		-	-	70	-	40	-	20	-	10
	Styrene-butadiene rubber		30	30	30	60	60	80	80	90	90
	Carbon Black		50	20	50	50	50	50	50	50	50
	Silica		-	30	-	-	-	-	-	-	-
	Spindle Oil		12	12	12	12	12	12	12	12	12
	Stearic Acid		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Zinc Oxide		4	4	4	4	4	4	4	4	4
	Vulcanization Accelerator		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
	Sulfur		3	3	3	3	3	3	3	3	3
Results	Mooney viscosity	-	62	82	59	56	55	55	56	54	54
	Ultimate strength	MPa	25	23	24	21	21	21	20	18	17
	Crack growth resistance	index	100	65	100	95	96	92	93	91	90
	tan δ	index	100	102	135	95	110	85	90	85	85
	Rolling resistance	index	100	100	103	99	101	96	99	97	97

* Modified natural rubber O-2 is a modified natural rubber graft-polymerized with 2-vinylpyridine.

Further, the results of the ultimate strength of the Additional Examples 8 and 9 and the Additional Comparative Examples 11 and 12 in Table I, the results of the ultimate strength of the Additional Examples 10 and 11 and the Additional Comparative Examples 13 and 14 in Table II, the results of the ultimate strength of the Additional Examples 12 and 13 and the Additional Comparative Examples 15 and 16 in Table III, and the results of the ultimate strength of the Additional Examples 1, 2 and 4 and the Additional Comparative Examples 17 and 18 in Table IV are summarized in the following graph, respectively.



(Summary)

As seen from Tables I, II, III and IV and the graph, when the grafting ratio of the modified natural rubber exceeds 5% by mass, the ultimate strength (fracture resistance) is largely deteriorated. Further, as from Tables I, II, III and IV, these unexpected results can be obtained in the tests using various modified natural rubbers.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements

and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 2010. 4. 2 Declarant: Makiko Yonemoto

Makiko Yonemoto